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Flexible Zr-MOFs as Bromine-Nanocontainers for Bromination Reactions under Ambient Conditions

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Dedicated to the 80th birthday for Prof. Academician Xin-Tao Wu

Abstract: A series of flexible MOFs (PCN-605, -606 and -700) are synthesized and applied to reversible bromine encapsulation and release. The chemical stability of these Zr-MOFs ensures the framework's integrity during the bromine adsorption, while the framework's flexibility allows for structural adaptation upon bromine uptake to afford stronger host-guest interactions and therefore higher bromine adsorption capacities. The flexible MOFs act as bromine-nanocontainers which elongate the storage time of volatile halides under ambient conditions. Furthermore, the bromine pre-adsorbed flexible MOFs can be used as generic bromine sources for bromination reactions with improved yields and selectivities under ambient conditions as compared with liquid bromine.

Metal-organic frameworks (MOFs), also referred to as porous coordination networks (PCNs), have been extensively investigated as a class of functional solid-state porous materials in the past two decades. Their structural and functional tunability has led to fascinating developments with respect to applications in gas storage and separation, chemical sensing, heterogeneous catalysis and so on.^[1] According to the literature, most reported MOFs with permanent porosities can be attributed to the second-generation of organic-inorganic hybrid porous materials.^[2] On account of their rigidity, this kind of MOF can maintain its original porosity even after the removal of guest molecules.^[3] However, flexible porous materials which can respond to various external stimuli via structural transitions while maintaining crystallinity are urgently desired for intelligent technology development.

Fortunately, the emergence of flexible MOFs (FMOFs) shines a ray of light on research for smart materials.^[4] FMOFs possess properties that are quite unique from rigid MOFs. Some

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fascinating examples includes the breathing phenomenon in response to guest adsorption as well as huge thermal expansions under thermal treatment.^[5] Intrinsic structural flexibility could lead to intriguing properties in gas storage, separation, and catalysis.^[6] Additionally, the pore environment of FMOFs can be changed by the breathing behavior which in turn modulates the catalytic activity.^[7] Therefore, tremendous efforts are made to construct FMOFs and understand their structure-property relationships.

Brominations are an important class of organic transformation essential for both laboratory research and modern industry. Liquid bromine is the most commonly-used bromination reagent with a high reactivity in bromination reactions. However, the safe storage and utilization of liquid bromine still remain challenging because of its highly volatile. Recently, a large number of rigid porous materials including MOFs were explored as iodine absorbents with relatively high adsorption capacities.^[8] Commendably, a redox-active MOF, Co₂Cl₂BTDD, was employed for the reversible capture and release of gaseous Cl₂ and Br₂.^[9]

FMOFs that undergo structure evolution upon guest uptake are particularly promising for adsorption and storage applications because this can lead to increased adsorption enthalpy, enhanced selectivity and high usable storage capacities. For example, the Long group developed a series of FMOFs for methane storage with intrinsic thermal management.^[10] The unique adsorption behavior of FMOFs motivates us to study their performance for liquid bromine adsorption and release. As we all know, most FMOFs are constructed through labile coordination bonds between low-valence metals and organic ligands, which are often sensitive to air moisture, aqueous solutions, acid, or base. However, halogens undergo partial hydrolysis to generate acidic species, which can induce framework decomposition. Therefore, we aim to develop chemically stable and inert MOFs with structural flexibility for specific halogen adsorption. It has been shown that porous MOFs based on Zr₆ clusters are stable towards acidic conditions due to the high-valent zirconium ions. Bearing this in mind, we focus on the design and synthesis of the Zr-based MOFs with structural flexibility.

To obtain flexible Zr-MOFs, a topology guided design was adopted. The Hupp group has computationally predicted a series of Zr-MOFs with different linkers and classified them by topology.^[11] Meanwhile, Smit et al also studied the predicted flexibility of MOFs based on its crystal topology.^[12] Accordingly, a high degree of flexibility is expected if Zr-MOFs adopt **bcu**, **flu**, or **scu** topologies. With this in mind, PCN-605, -606, and -700 systems were designed from the topological viewpoint and their flexibilities were evaluated. For comparison, the bromine adsorption performance of a rigid MOF (UiO-67) with similar porosity was also investigated.

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Figure 1. Structural comparison of UiO-67, PCN-700, PCN-605 and PCN-606. (a) UiO-67 with **fcu** topology is composed of 12-connected Zr_6 clusters and linear ligands while PCN-700 with **bcu** topology is composed of 8-connected Zr_6 clusters and dimethylated linear ligands. (b) The tetratopic ligand with various substituents adopt a T_d or D_{2h} symmetry, respectively, and further bridges the 8-connected Zr_6 clusters to form PCN-605 and -606 series with **flu** or **scu** topologies.

The **bcu** structure consisting of 8-connected Zr₆ clusters and linear linkers was reported by our group as PCN-700.^[7a] It can be regarded as a structural derivative of UiO-67 by partial elimination of linkers. UiO-67 with **fcu** topology possesses a rigid framework, which is constructed by 12-connected Zr₆ clusters and linear BPDC ligands. However, the introduction of the dimethylated linear carboxylate ligands (Me₂-BPDC) gives rise to the deduction form of the **fcu** topology by exclusion of four linkers in the equatorial plane of the octahedral cluster (Figure 1a). The symmetry of the crystal is reduced from cubic to tetragonal with the topology of the framework changing from **fcu** to **bcu** and thus the framework flexibility emerges.

Zr-MOFs with **flu** topology were also documented, however, the flexibility is rarely studied. For example, UMCM-312, reported by Matzger and coworkers, was composed of 8-connected Zr₆ clusters and tetratopic linkers with a tetrahedral geometry.^[13] The rotations and deformations of the tetratopic ligands resulting from biphenyl groups can bring about flexibility in the framework. Introducing bulky substitutes on the 2,2'-positions of biphenyl moieties could potentially restrict the rotations and deformations of linkers and thereby tune the flexibility of the frameworks. In light of this, two tetratopic ligands with different substitutes, 2,2'-H-H₄TPCB, and 2,2'-OH-H₄TPCB were selected, giving rise to the PCN-605 series (which was also termed UMCM-312 when 2,2'-H-H₄TPCB was used). In PCN-605, the tetratopic ligand adopts a T_d symmetry due to the free rotation of the C-C bond between the two phenyl rings which is similar to the role of H₄MTBC in PCN-521.^[14] Thus, if we simplify the ligands as 4-connected nodes and the Zr₆ clusters as 8-connected nodes, PCN-605 adopts the {4,8}c **flu** network with the topological point symbol of {4¹².6¹².8⁴}{4⁶}2.^[15]

In order to obtain FMOFs with **scu** topology, a planar ligand should be utilized as the linker. On the basis of our previous work, a series of 4,4'-substituted ligands of H₄TPCB, 4,4'-OMe-H₄TPCB, 4,4'-OH-H₄TPCB, and 4,4'-NH₂-H₄TPCB were selected to maintain the coplanar nature of inner biphenyl fragments. Theoretically, a redox balance exists for the hydroxyl or amino group functionalized biphenyl moieties, which will lead to the coplanar configuration of the biphenyl (Figure S1). Solvothermal reactions of the planar tetratopic ligands and ZrCl₄ give another type of three-dimensional framework termed the PCN-606 series. Single-crystal X-ray diffraction experiments at 100 K revealed that PCN-606 crystallized in the orthorhombic space group *Cmmm*. As expected, the inner biphenyl ring of the ligand is inclined to be coplanar because of the presence of the two substituents on the tetracarboxylate ligands. These series of tetratopic ligands adopt

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 D_{2h} symmetry rather than T_d symmetry, which has been observed in previous research.^[16] However, the outer benzoate group is far from coplanar to the biphenyl core with a dihedral angle of 54.28°. Finally, a large rhombic one-dimensional channel of approximately 15 × 30 Å was observed along the crystallographic *c* axis. From the topological point of view, if the ligands were regarded as 4-connected nodes and the Zr₆ clusters as 8connected nodes, PCN-606 adopts the {4,8}-c **scu** network with the topological point symbol of {4¹⁶.6¹²}{4⁴.6²}₂ (Figure 1b).

Because of the flexibility of the frameworks, activation of the FMOFs using conventional methods (solvent exchange followed by degas under high temperatures) failed. Thus, super-critical CO_2 was used to active the samples in order to confirm the permanent porosity of these flexible MOFs. As shown in Figure S4, PCN-606-OH shows the highest N₂ adsorption amount of 630 cm³ g⁻¹, while PCN-606-OMe exhibits the lowest N₂ uptake of 280 cm³ g⁻¹ at 77 K (1 atm).



Figure 2. Structure of (a) PCN-605-H, (b) PCN-606-OMe, (c) PCN-700, and (d) UiO-67 before (left) and after (right) bromine adsorption. The one-dimensional channels of the flexible MOFs expand after bromine adsorption while the channels in rigid MOFs remain unchanged. Color codes: gray C, red O, blue Zr, green Br.

Considering that the hydroxyl and amino groups may be sensitive to bromine, two analogues without these functional groups, PCN-605-H and PCN-606-OMe, were used to capture bromine. A fresh, crystalline sample of PCN-605-H, PCN-606-OMe, PCN-700, and UiO-67 were immersed into a 1 mol•L⁻¹ cyclohexane solution of liquid bromine formed after solvent exchange with acetone and then cyclohexane for three times respectively. The sample color gradually changed from colorless to yellow and then dark red as bromine diffused into the pores of the MOF. UV-Vis analysis also indicated that the concentration of bromine in cyclohexane decreased with time (Figure S2). According to the UV-Vis results, the total bromine uptake of PCN-605-H, PCN-606-OMe, PCN-700, and UiO-67 are 4.2, 3.7, 2.6, and 1.9 g•g⁻¹, respectively. As expected, these three FMOFs

show higher bromine uptake capacities than that of the rigid MOF, because the FMOFs may adopt larger pore configurations when immersed into the bromine solution. Luckily, single crystal data of the four MOFs were also measured after bromine adsorption, which were named PCN-605-H-Br, PCN-606-OMe-Br, PCN-700-Br, and UiO-67-Br. It should be noted that free Br atoms can be located in the pores of the FMOFs but cannot be located in UiO-67 because of the high symmetry. This single crystal data revealed that bromine molecules were encapsulated into the pores of the MOFs. Interestingly, the crystallographic a axis of the three FMOFs (c axis for PCN-700-Br) expand with coefficients of 4.5%, 3.6%, and 1.2% respectively after bromine adsorption compared with the as-synthesized ones, indicating the expansion of the pores in the FMOFs. However, the unit cell parameters of the rigid framework UiO-67 remained almost unchanged (Figure 2).

Bromination reactions should typically be performed under low temperatures in order to improve the reaction selectivity and efficiency when using liquid bromine. The slow release of bromine from the MOFs' pores into the reaction system may also decrease the bromination rate, which is similar to dropwise addition of bromine under low temperature. In order to verify the above idea, the four bromine pre-absorbed MOFs materials were tested as halogenation agents for binaphthol under ambient condition. The reaction systems were vibrated on a vortexer overnight and the bromination reaction results are listed in Table 1.

Table 1. Bromination of binaphthol utilizing the bromine pre-absorbed MOFs. $\ensuremath{^a}$



^a The MOF-loaded bromine was added in 20% excess. The reaction mixture were vibrated overnight at room temperature before worked up.

Surprisingly, the efficiency of binaphthol bromination using bromine pre-absorbed FMOFs are much higher than the rigid MOF and even higher than directly using liquid bromine under ambient conditions. Furthermore, PCN-606-OMe-Br and PCN-700-Br show excellent repeatability in bromine capture and release capacities with bromination yields of 75% and 62% after three cycles of adsorption-bromination tests, respectively. This indicates that these two FMOFs show promise in practical applications. It should be noted that the volatilization of the bromine in FMOFs is much slower than that in the liquid state at room temperature. Almost all of liquid bromine was gasified within one hour while more than 80 percent of bromine remained in FMOFs after 24 hours, when the same amount of bromine in liquid state and pre-absorbed MOFs were placed under ambient conditions.

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In addition, PCN-606-OMe-Br and PCN-700-Br were also used for bromination of biphenols and anilines under ambient conditions. As shown in Table S2, the bromination yields of 4,4'biphenol and *p*-anisidine are much higher than would be obtained using liquid bromine, indicating that these bromine pre-absorbed FMOFs can be used as generic bromine sources for bromination reactions.^[17]

In conclusion, a series of FMOFs have been synthesized on the basis of linear or tetratopic organic ligands and 8-connected Zr_6 clusters. Taking advantage of the flexible frameworks, these materials show higher bromine adsorption capacities than the rigid MOF. Additionally, the bromine pre-adsorbed FMOFs can be utilized as bromine sources under ambient conditions, and the efficiency of the bromination reaction for organic starting molecules can be significantly improved.

The flexible and chemically stable Zr-MOFs developed in this work shall provide versatile platforms for the study of fundamental science and applications in gas storage, separation, drug delivery and catalysis.

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A series of flexible Zr-based metalorganic frameworks (MOFs) are designed and synthesized under a topology guided strategy. These MOFs show significant structural transformation during desolvation and bromine adsorption. In addition, the bromine pre-adsorbed flexible MOFs can be used as generic bromine sources for bromination reactions with improved yields and selectivities under ambient conditions as compared with liquid bromine.



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